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THE INFLUENCE OF CHARGE EFFECT ON THE GROWTH OF HYDROGENATED AMORPHOUS SILICON BY THE HOT-WIRE CHEMICAL VAPOR DEPOSITION TECHNIQUE

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ABSTRACT: We observe at lower substrate temperatures that the scatter in the dark conductivity on hydrogenated amorphous silicon (a-Si:H) films grown on insulating substrates (e.g., Corning 7059 glass) by the hot-wire chemical vapor deposition technique (HWCVD) can be five orders of magnitude or more. This is especially true at deposition temperatures below 350°C. However, when we grow the same materials on substrates with a conductive grid, virtually all of our films have acceptable dark conductivity ($< 5 \times 10^{-10}$ S/cm) at all deposition temperatures below 425°C. This is in contrast to only about 20% of the materials grown in this same temperature range on insulating substrates having an acceptable dark conductivity. We estimated an average energy of 5 eV electrons reaching the growing surface in vacuum, and did additional experiments to see the influence of both the electron flux and the energy of the electrons on the film growth. Although these effects do not seem to be important for growing a-Si:H by HWCVD on conductive substrates, they help us better understand the important parameters for a-Si:H growth, and thus, to optimize these parameters in other applications of HWCVD technology.

Keywords: Vienna Conference - 1: HWCVD - 2: Conductivity - 3: Electron emission.

1. INTRODUCTION

Hydrogenated amorphous silicon (a-Si:H) grown by the traditional plasma-enhanced chemical vapor deposition (PECVD) technique is now used in numerous commercial electronic applications. After more than 20 years of research, this technique is mature relative to other growth methods. It fabricates device quality a-Si:H materials and devices, and is a controllable process that can be scaled up. A major drawback is the slow deposition rate for producing the high quality material, which limits the throughput for device manufacturing. Increased deposition rate can bring the cost down. Clearly there is a demand for alternative deposition to grow high-quality material at higher deposition rates. A recent report of achieving 9.8% [1] initial solar cell efficiency at 17 Å/sec deposition rate in the small scale using HWCVD suggests that this could be a good candidate. The advantages of the HWCVD relative to PECVD include: 1. The growth rate for high-quality a-Si:H can be much higher [2] (more than 10 times); 2. The a-Si:H produced by HWCVD is more stable [3]; and 3. The structure of the high-quality a-Si:H is different and more dense [4]. While the process of HWCVD is very easy to operate, the technique is not as well understood. HWCVD materials can be superior to PECVD materials, but the variation in material properties from laboratory to laboratory and over the course of a batch of depositions is much greater. In this paper, we report the observation of non-uniform electronic properties of a-Si:H material grown at certain conditions [5], present an overview of the HWCVD process, speculate on the role of the electrons emitted from the filament on the material quality, and propose ways to grow films with uniform electronic properties.

2. EXPERIMENTAL

We deposit a-Si:H films on 1 in x 1 in glass (Corning 7059 glass) in a HWCVD reactor. The standard conditions for growing a-Si:H film use 20-50 sccm of SiH₄ and 10 mT pressure. All the films are about 1 µm thick. Here we give a brief description of the HWCVD deposition technique. We

use a straight or spiral tungsten filament with a diameter of 0.5 mm and place it 4-5 cm below the substrate. A spiral shaped filament has proven to better accommodate to the thermal stress due to the heating and cooling of the filament, enabling an increase in the filament lifetime. A typical lifetime of the filament varies from 5 to 9 hours depending on deposition conditions. Tungsten reacts with SiH₄ at lower filament temperatures, which forms alloy and ultimately causes the filament to break. The filament itself is a research subject, and we do not discuss it in this paper. The filament is heated by an AC or DC current (14 A) to about 1900 °C. A process gas, such as silane, passes by the hot-filament, dissociates, and leads to a-Si:H deposition on the substrate.

We use two different methods to heat the substrate, this leads to two different HWCVD reactors. Fig. 1 shows the schematic diagram of the two HWCVD reactors. Our first reactor utilized a six-way cross (we name it the cross reactor, see Fig 1a.). The substrate is mounted on the bottom of the sample holder and an external heater heats the sample holder and the substrate. The temperature of the substrate is monitored using a thermocouple attached to the outside of the top flange. In this design the top part of the cross is hot and the rest is cold. The filament is placed below the substrate, and the direction of gas flow is perpendicular to the filament. The details of this HWCVD reactor are reported elsewhere [6]. Our new reactor design places a stainless-steel tube inside the vacuum chamber (we name it the tube reactor, see Fig. 1b.), and the tube is heated using a resistive heating wire wrapped around the outer tube. Substrates are placed in the middle of the tube and can be transported to the load lock. This design produces an isothermal region in the middle of the tube and ensures the uniformity of the substrate temperature. The filament is placed inside the tube and below the substrate, and parallel to the gas flow.

We measure dark conductivity vs. spatial position on an a-Si:H film using a Keithley electrometer model 619 or 6517a. The thickness of the film is measured using a Tencor Instrument Alpha-Step 200 profilometer. For charge-collection measurement, we use an electrically isolated stainless-steel plate as a collector, position it next

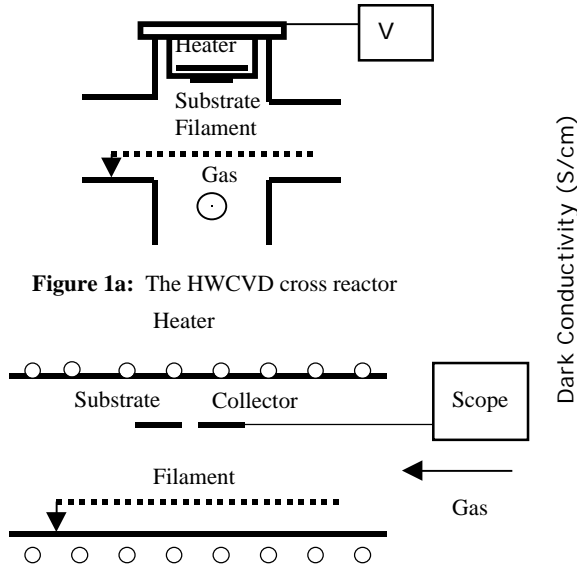


Figure 1a: The HWCVD cross reactor

Figure 1b: The HWCVD tube reactor. Tube is side the vacuum chamber which is not shown.

to the substrate in the tube reactor, and use an oscilloscope to monitor the charge collected by the plate during the time the filament is on as shown in Fig. 1b.

3. RESULTS AND DISCUSSION

We originally observe at a lower substrate temperature (220°C), that the scatter in the dark conductivity on films grown on insulating substrates (e.g., Corning 7059 glass), by the HWCVD in the cross reactor can be as much as five or more orders of magnitude. Fig. 2 shows the mapping of the dark conductivity across a 1 in x 1 in substrate. This effect is enormous: the film at the edge of the substrate has a typical low dark conductivity while the value in the middle is almost 5 orders of magnitude higher, even on such a small scale as a 1 in x 1 in substrate. To understand this behavior we have concentrated on two ideas. The first one is the non-uniformity of the temperature distribution across the substrate, where the temperature in the center differs from that on the edge. It is well known that substrate temperature does affect the quality of the film. The results of this research have been published elsewhere [5]. The idea investigated in this paper deals with the charging of the insulating substrate by electrons emitted from filament. As we shall show that the charge on the edge is likely to discharge while the charge in the center which remains will affect the film quality. We will describe and demonstrate how electrons are released from the hot filament, how the electrons interact with process gas in the gas phase, and how the electrons contribute to reactions at the substrate surface.

The filament is directly heated by passing a current. The hot filament provides a heat source and also a source of electrons. Without the presence of process gas, the HWCVD reactor is just like a vacuum tube. Based on the vacuum-tube theory, the emission current density J_c follows

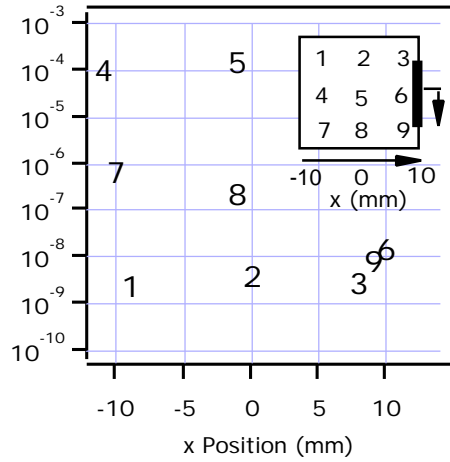


Figure 2: The mapping of dark conductivity of a-Si:H on glass substrate at 220°C substrate temperature. Inserted figure is the glass substrate and the numbers indicate the positions on the film that conductivity be measured. The dark strip on the side is grounded metal clips to hold substrate.

Richardson's law:

$$J_c = A_c T^2 \exp(-E_w/kT), \quad (1)$$

where A_c is a constant which is a function of the material, E_w is the work function of the material, and T is the emission temperature. J_c increases with increasing filament temperature.

We use tungsten as the filament material. There is a report using Tantalum as the filament material [7]. The advantages of tungsten are low cost and high filament temperature. For tungsten, A_c equals 60 A/cm²K² and E_w equals 4.5 eV. At 2200 K, J_c equals 14.4 mA/cm², corresponding to 9×10^{16} electrons/sec cm².

We measure the electrons coming out of the hot filament in the tube reactor. The setup is described in Fig. 1b. Electrons emitted from the filament pass through the vacuum region, hit the isolated collector, and cause a current flow to the ground. The signal is monitored using an oscilloscope. Fig. 3a shows the voltage applied to the filament as a function of time, and Fig. 3b shows the monitored charge signal. For a DC current (DC+) with the filament voltage positive relative to the collector, there is no signal. Electrons are suppressed by the high potential at the filament relative to the collector and no electrons pass through the vacuum region. For a DC current (DC-) with the filament voltage negative to the collector, there is a constant negative signal. Electrons accelerate in the vacuum region and reach the collector. For an AC current, the collected signal becomes more complicated: the signal varies with time. As previously mentioned, there are no signals for every positive voltage cycle. For every negative voltage cycle, there is a negative signal, but with two humps. These two humps are due to magnetic field changes

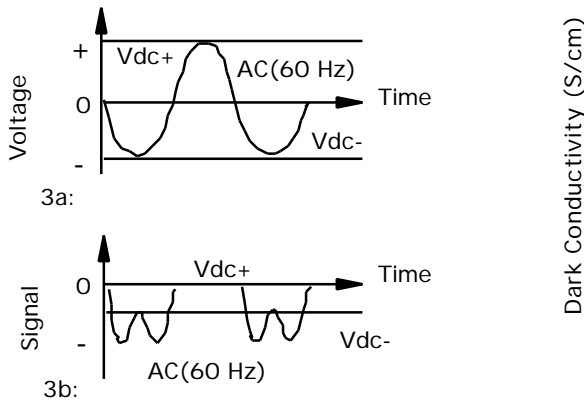
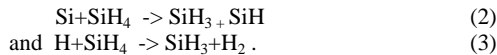


Figure 3: Results of charge-collection experiment. The voltage arrow applies to the filament and the signal arrow represents the oscilloscope monitoring.

in response to the electric field varying with time. The magnetic field influences the emission of electrons from the filament and also the trajectory of the electrons entering in the vacuum. An additional complication is that the electron distribution in the vacuum is not uniform because of the voltage drop across the filament. In our system, a typical voltage drop on the filament is about 8-10 V. We estimate that the average energy which electrons reach the substrate is about 4-5 eV in vacuum.

We feel there is a need to better understand the mechanism of the HWCVD technique. HWCVD is a complicated process, illuminating the substrate with heat, light, and electrons. A simplified model could be that HWCVD is composed of thermal CVD, photo-CVD, and PECVD.

The principal mechanism of HWCVD deposition is that SiH_4 molecules hit the hot filament and decompose into one Si and four H, and are evaporated into the reaction region. These atoms collide with other SiH_4 that does not hit the hot filament. The reactions can be described as:



It is these Si containing radicals which reach the substrate and make a deposition. The interested reader can find more information in E. Molenbroek's thesis [8].

We measure the light intensity at the substrate surface is about 3-4 Suns ($300\text{-}400 \text{ mW/cm}^2$) using a crystal Si photodiode in our reactor configuration. Most photons are in infrared region because the filament temperature is about 2200 K. We do not discuss how the light interact with gases and at the substrate surface in this paper.

The electrons interaction with process gases is unavoidable, because there are high electron densities at the surface of the filament. The electron reaction with SiH_4 is well-known, for example:

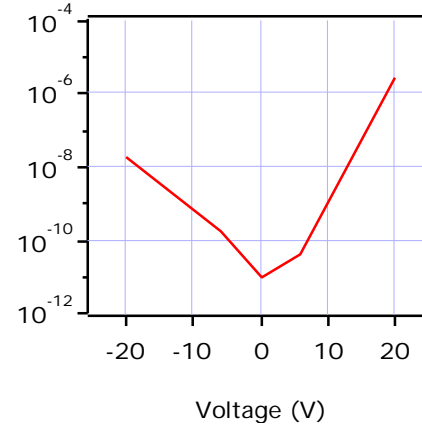
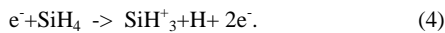


Figure 4: The effect of bias on the a-Si:H film quality. The represents the value of many sample data.

We did a preliminary study of the effect of voltage bias on the substrate on the film quality in the cross reactor. We float the substrate by isolating the top flange with a Viton O-ring instead of the copper gasket and use nylon bolts instead of stainless-steel bolts. We apply the DC voltage directly to the top flange relative to the ground (see Fig. 1a.). The substrate is attached to the flange. The drawback of this arrangement is that base pressure is higher than our conventional configuration.

It is worthy to note that electrons even without any voltage bias have an average energy of 5 eV. Hence, applying a bias will increase or decrease the electron energy. Fig. 4 shows the film dark conductivity as a function of bias in a range from -20 to 20 V. It shows that bias does affect the film quality. It seems that the best-quality material is near zero bias, while high bias increases the dark conductivity. Certainly a better bias experiment design, such as a diode or a triode electrode is needed to re-confirm this effect.

Finally, we report on our observations of how electrons react at the substrate surface. We design two experiments to test if it is the electrons coming from the filament that influence the electronic properties of growing a-Si:H films. One uses a metal grid on an insulating substrate. The idea is to have electrons discharge through the grid. The other experiment involved increasing the substrate temperature. The conductivity of the film increases with the temperature, and electrons can be discharged more easily [5].

We put two different substrates into the tube reactor. One is a plane, 25 mm x 25 mm Corning 7059 glass and the other is a 7059 glass, with an Ag grid put on the surface using a silver epoxy. The grid divides the substrate into nine areas of open glass, approximately 7 mm x 7 mm, with a conductive border around all four outside edges of the open area. After growing a film simultaneously on both substrates, we measure the conductivity on both substrates at similar locations (nine positions on each). Fig. 5 shows the dark conductivity in the grid sample made at 220°C substrate temperature as a function of its position. The scatter of the dark conductivity is much suppressed compared with the data presented in Fig. 2. The variation is

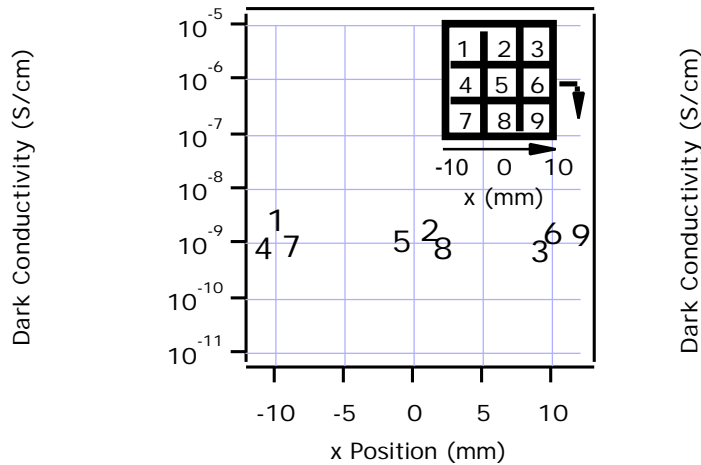


Figure 5: The effect of Ag grid on the dark conductivity. Sample is made at 220°C substrate temperature.

limited to one order of magnitude. This indicates that the grid does help to discharge the substrate.

We also find that our samples made at above 350°C substrate temperature have much less scatter in the dark conductivity. Fig. 6 shows the results of dark conductivity of a sample made at 350°C. The results are consistent with our premise that electrons charge the insulating substrate. At higher substrate temperature, the conductivity of the film increases enough to enable the electrons to be discharged from the film.

While the effects we report do not seem to be important for growing a-Si:H by HWCVD on conductive substrates or at higher substrate temperatures, it helps us better understand the important parameters for a-Si:H growth and thus to optimize these parameters for other applications of the HWCD technology.

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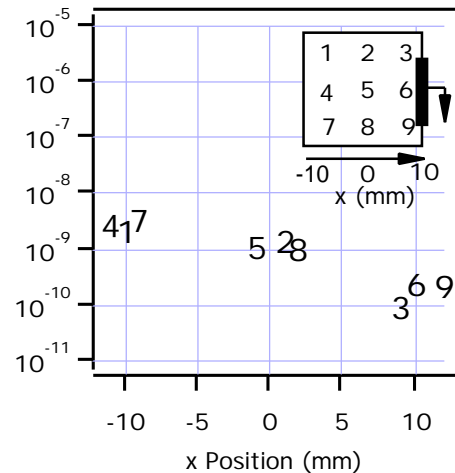


Figure 6: The effect of higher substrate temperature (350°C) on the dark conductivity of a-Si:H material. The dark strip on the side is grounded metal clips to hold substrate.

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